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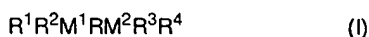
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(54) **Hydroformylation process**

(57) A process for the hydroformylation of ethylenically unsaturated compounds with carbon monoxide and hydrogen in the presence of a catalyst system comprising

- a) a source of platinum group metal cations;
- b) a source of non-halide anions;
- c) a source of at least one bidentate ligand of the formula



wherein M^1 and M^2 independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent bridging group containing from 1-4 atoms in the bridge, R^1 and R^2 independently represent a substituted or unsubstituted hydrocarbyl group, or together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M^1 , and R^3 and R^4 independently represent a substituted or unsubstituted hydrocarbyl group, or together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M^2 ; and
d) a source of halide anions chosen from the group of chloride, iodide and bromide and mixtures thereof, characterised by the additional presence of water, in an amount of more than 0.6 wt% based on the total of the reaction mixture and up to its solubility limit under the reaction conditions.

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Description

[0001] The invention relates to a process for the hydroformylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and hydrogen in the presence of a catalyst.

[0002] The hydroformylation of ethylenically unsaturated compounds to form aldehydes and/or alcohols, is of considerable industrial importance. The process has been in commercial operation for decades and over the years much development work has been done to optimize the reaction conditions, the catalyst system and the equipment. Although significant progress towards higher yield and product selectivity has been made, further improvement of the process is still needed.

[0003] In EP-B 0 495 547 there is disclosed a monocarbonylation process whereby the catalyst system comprises a source of palladium cations, a source of anions, and a bidentate diphosphine as defined below. In hydroformylating olefins, the activity and selectivity of this catalyst system is still not entirely satisfactory.

[0004] In WO 95/05354 there is disclosed a hydroformylation process whereby the catalyst system comprises a source of platinum group metal cations, a source of anions other than halide anions, a source of bidentate ligands as defined below and a catalyst promoter comprising a source of halide anions in a molar ratio halide anion: platinum group metal cation of at most 3:1. It is shown that the presence of the halide ion accounts for a considerably enhanced activity and selectivity of the process towards the desired alcohol products. However, the process according to WO 95/05354 also appears to be exceedingly sensitive to small variations in halide ion concentration, the positive effect of which having a sharp peak at a molar ratio to the cation of about 0.4:1. In Examples 10-12 of WO 95/05354 tin chloride was the promoter used and water was added to an amount of 0.6 wt%, calculated on the total of the reaction mixture. However, any particular effect of the water was not recognised and cannot be deduced from this document.

[0005] It has now been found that water, when added in an amount of more than 0.6 wt% based on the total of the reaction mixture and up to its solubility limit in the reaction mixture under the reaction conditions and in particular up to 3 wt%, acts as a strong co-promoter with the halide anion.

[0006] Accordingly, the present invention relates to a process for the hydroformylation of ethylenically unsaturated compounds with carbon monoxide and hydrogen in the presence of a catalyst system comprising

a) a source of platinum group metal cations;

b) a source of non-halide anions;

c) a source of at least one bidentate ligand of the formula



wherein M^1 and M^2 independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent bridging group containing from 1-4 atoms in the bridge, R^1 and R^2 independently represent a substituted or unsubstituted hydrocarbyl group, or together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M^1 , and R^3 and R^4 independently represent a substituted or unsubstituted hydrocarbyl group, or together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M^2 ; and

d) a source of halide anions chosen from the group of chloride, iodide and bromide and mixtures thereof, characterised by the additional presence of water, in an amount of more than 0.6 wt% based on the total of the reaction mixture and up to its solubility limit under the reaction conditions.

[0007] Preferably, the molar ratio between the halide anions and the platinum group metal is between 0.02:1 and 3:1.

[0008] Preferably, the amount of water is between 0.7-3.0 wt%, based on the total of the reaction mixture.

[0009] In the present specification the metals of the platinum group are defined as the metals with the atomic numbers 28, 46 and 78, i.e. nickel, palladium and platinum. Of these, palladium and platinum are preferred.

[0010] Examples of suitable metal sources are platinum or palladium compounds such as salts of palladium and nitric acid, sulphuric acid or sulphonic acids, salts of platinum or palladium and carboxylic acids with up to 12 carbon atoms, palladium- or platinum complexes, e.g. with carbon monoxide or acetylacetonate, or palladium combined with a solid material such as an ion exchanger or carbon. Palladium(II) acetate and platinum(II) acetylacetonate are examples of preferred metal sources.

[0011] As anion source, other than halide anions, any compound generating these anions may be used. Suitably, acids, or salts thereof, are used as source of anions, for example any of the acids mentioned above, which may also participate in the salts of the metals of the platinum group.

[0012] In the catalyst systems of the invention, preferably strong acids are used as anion source, i.e. acids having a pKa value of less than 3, preferably less than 2, measured in aqueous solution at 18 °C. The anions derived from these acids are non-coordinating or weakly coordinating with the metals of the platinum group.

[0013] Typical examples of suitable anions are anions of phosphoric acid, sulphuric acid, sulphonic acids and halogenated carboxylic acids such as trifluoroacetic acid.

[0014] Sulphonic acids are in particular preferred, for example methanesulphonic acid, trifluoromethanesulphonic acid, tert-buthanesulphonic acid, p-toluenesulphonic acid and 2,4,6-trimethylbenzenesulphonic acid.

5 **[0015]** Complex anions are also suitable, such as the anions generated by a combination of a Lewis acid such as BF_3 , AlCl_3 , SnF_2 , $\text{Sn}(\text{CF}_3\text{SO}_3)_2$, SnCl_2 or GeCl_2 , with a protic acid, such as a sulphonic acid, e.g. $\text{CF}_3\text{SO}_3\text{H}$ or $\text{CH}_3\text{SO}_3\text{H}$ or a hydrohalogenic acid such as HF or HCl , or a combination of a Lewis acid with an alcohol. Examples of such complex anions are BF_4^- , SnCl_3^- , $[\text{SnCl}_2 \cdot \text{CF}_3\text{SO}_3]^-$ and PF_6^- .

10 **[0016]** In bidentate ligands of formula (I), i.e., component c of the catalyst system, M^1 and M^2 are preferably the same and, more preferably, are both phosphorus atoms, in which case the ligands are bisphosphines.

[0017] In the bridging group, represented by R, typically all bridging groups are carbon atoms. Preferably the bridging group contains two or three, more preferably two, carbon atoms in the bridge. Thus, exemplary organic bridging groups R are $\text{CH}_2\text{-CH}_2$ and $\text{CH}_2\text{-CH}_2\text{-CH}_2$.

15 **[0018]** The bivalent (substituted) cyclic group, represented by R^1 together with R^2 , in general comprises at least 5 ring atoms and preferably contains from 6 to 9 ring atoms. More preferably the cyclic group contains 8 ring atoms. Substituents, if any, are usually alkyl groups having from 1 to 4 carbon atoms. As a rule, all ring atoms are carbon atoms, but bivalent cyclic groups containing one or two heteroatoms in the ring, such as oxygen- or nitrogen, atoms are not precluded. Examples of suitable bivalent cyclic groups are 1,4-cyclohexylene, 1,4-cycloheptylene, 1,3-cycloheptylene, 1,2-cyclooctylene, 1,3-cyclooctylene, 1,4-cyclooctylene, 1,5-cyclooctylene, 2-methyl-1,5-cyclooctylene, 2,6-dimethyl-1,4-cyclooctylene and 2,6-dimethyl-1,5-cyclooctylene groups.

20 **[0019]** Preferred bivalent cyclic groups are selected from 1,4-cyclooctylene, 1,5-cyclooctylene, and methyl (di)substituted derivatives thereof.

[0020] Mixtures of ligands comprising different bivalent cyclic groups may be used as well, e.g. mixtures of ligands with 1,4-cyclooctylene and ligands with 1,5-cyclooctylene groups.

25 **[0021]** In the ligands of formula (I), R^3 and R^4 may independently represent various non-cyclic or cyclic groups, optionally substituted with substituents such as alkoxy groups with 1 to 4 carbon atoms, halogen atoms or (C_1 to C_4 alkyl)amino groups.

30 **[0022]** Examples are alkyl groups such as ethyl, isopropyl, sec-butyl and tert-butyl groups, cycloalkyl groups such as cyclopentyl and cyclohexyl groups, aryl groups such as phenyl and tolyl groups and bivalent groups such as a hexamethylene group. However, preferably R^3 , together with R^4 represents a bivalent cyclic group, in particular the same group as the group represented by R^1 together with R^2 , in which case the two free valencies of the bivalent cyclic group are, of course, linked to M^2 , instead of M^1 . Thus, preferred bidentate ligands of formula (I) are 1,2-bis(1,4-cyclooctylenephosphino)ethane, 1,2-bis(1,5-cyclooctylenephosphino)ethane and mixtures thereof.

35 **[0023]** For the preparation of the bidentate ligands, reference is made to known techniques, for example the method disclosed in GB-A-1,127,965.

[0024] The quantity in which the catalyst system is used, is not critical and may vary within wide limits. Usually amounts in the range of 10^{-8} to 10^{-1} , preferably in the range of 10^{-7} to 10^{-2} mole atom of platinum group metal per mole of ethylenically unsaturated compound are used. The amounts of the participants in the catalyst system are conveniently selected such that per mole atom of platinum group metal from 0.5 to 10, preferably from 1 to 6 moles of bidentate

40 ligand are used, from 0.5 to 15, preferably from 1 to 8 moles of anion source or a complex anion source.

[0025] The molar ratio between halide anions and platinum group metal cations is preferably not more than 3:1. If larger amounts of halide anions are present, the activity of the catalyst system tends to be adversely affected, presumably because of coordination occurring between palladium and halide moieties.

45 **[0026]** Preferably, the molar ratio between halide anions and platinum group metal cations is at most 2:1, more preferably less than 1:1, for instance from 0.02:1 to 1:1.

[0027] As source of halide anions any compound generating halide anions under the reaction conditions may be used.

[0028] Recommended are inorganic compounds such as hydrogen halides, e.g. HCl , HBr and HI and metal halides, e.g. NaCl , MgBr_2 , ZnCl_2 , ZnI_2 , KBr , RbCl , CsCl , CsI , MgI_2 and CuCl .

50 **[0029]** Another category of recommended sources of halide anions consists of halogen containing organic compounds which are capable of providing halide anions to the reaction medium. Suitable are for example organic phosphonium halides, such as triarylalkyl phosphonium chloride and halogen containing aromatic compounds such as 5-halobenzoic acids, e.g. 5-chlorobenzoic acid, 2,5-dichlorobenzoic acid, 2,3,5-tri-iodobenzoic acid, 3,5-diiodobenzoic acid, m-halophthalic acids and esters thereof.

55 **[0030]** Catalyst promoters comprising a source of chloride anions are in particular preferred.

[0031] The ethylenically unsaturated compound, used as starting material, is preferably an olefin having from 2 to 30 carbon atoms per molecule, or a mixture thereof. They may comprise one or more double bonds per molecule. Preferred are internal olefins having from 4 to 24 carbon atoms, or mixtures thereof. Such olefin mixtures are commercially

readily available, for example as products of a process for the oligomerization of ethylene, followed by a double bond isomerization and disproportionation reaction. In the process of the invention, these internal olefins, usually mixtures of linear internal olefins with 6 to 20 carbon atoms per molecule, or closer boiling fractions of such mixtures, can be hydroformylated at high rates and an almost complete conversion. Examples are mixtures of linear internal C₆ to C₈ olefins, and of linear internal C₁₀ to C₁₄ olefins.

[0032] Substituted olefins may also be used, for example unsaturated carboxylic acids, esters of such acids, or unsaturated esters of carboxylic acids, e.g. allyl-acetate.

[0033] If desired, branched olefins such as propene trimer or isomeric butene dimers ("DIMERSOL" a trademark) may be used, but the hydroformylation product will then, of course, contain branched structures as well.

[0034] Also, olefinically unsaturated polymeric feedstock, such as atactic polyolefins like 'Shube's' (mixture of oligomers of C₁₆-olefins), "NAPVIS" and "HYVIS" (trade-marks for low molecular weight polyisobutylene) and styrene-butadiene (block)copolymers may be converted into interesting alcohols (as intermediates to synthetic lubricants, functionalized additives, etc.).

[0035] Finally, alpha-olefins, such as 1-octene and propene, and diolefins, such as norbornadiene, dicyclopentadiene, 1,5-hexadiene and 1,7-octadiene may be used. The diolefins will of course yield (predominantly) a dihydroformylated product, although also mono-hydroformylated may be formed.

[0036] Hydrogen and carbon monoxide may be supplied in equimolar or non-equimolar ratios, e.g. in a ratio within the range of 8:1 to 1:4, typically 4:1 to 1:2. Preferably they are supplied in a ratio within the range of 3:1 to 1:2.

[0037] The hydroformylation can be suitably carried out at moderate reaction conditions. Hence temperatures in the range of 50 to 200 °C are recommended, preferred temperatures being in the range of 70 to 160 °C. Reaction pressures in the range of 5 to 100 bar are preferred, lower or higher pressures may be selected, but are not considered particularly advantageous. Moreover, higher pressures require special equipment provisions.

[0038] In the process of the invention, the ethylenically unsaturated starting material and the formed hydroformylation product may act as reaction diluent. Hence, the use of a separate solvent is not necessary. Conveniently, however, the hydroformylation reaction may be carried out in the additional presence of a solvent. As such, saturated hydrocarbons, e.g. paraffins and isoalkanes are recommended and furthermore alcohols, preferably having from 4 to 10 carbon atoms per molecule, such as butanol, ethylhexanol-1, nonanol-1, or in general terms the alcohols formed as hydroformylation product; ethers such as 2,5,8-trioxanonane (diglyme), diethylether and anisole, and ketones, such as methylbutylketone.

[0039] In earlier hydroformylation processes, such as the process according to EP-A-0,495,547, the use of an alcohol as solvent was often considered undesirable, since the used hydroformylation catalysts were also catalytically active in the formation of esters in a reaction involving an olefin, carbon monoxide and the solvent alcohol. However, the catalyst systems of the present invention in view of their high selectivity towards the desired hydroformylation product, allow the use of alcohols as solvent.

[0040] Solvents containing strong polar groups are in particular preferred if the unsaturated starting material has a relatively low molecular weight, i.e., if ethylenically unsaturated compounds having from 5 to 7 carbon atoms are used.

[0041] For the hydroformylation of higher molecular weight unsaturated compounds, e.g. olefins having from 10 to 18 carbon atoms the use of less polar inert solvents will usually be satisfactory.

[0042] Solvents, comprising or substantially consisting of sulphones are preferred. Sulphones are in particular preferred, for example dialkylsulphones such as dimethylsulphone and diethylsulphone and cyclic sulphones, such as sulfolane (tetrahydrothiophene-2,2-dioxide), sulfolene, 2-methylsulfolane and 2-methyl-4-ethylsulfolane.

[0043] Sulfolane has proved to be a most effective solvent for the formation of a multiphase liquid reaction medium.

[0044] Mixtures of solvents may also be used, for example a mixture of a sulphone with a protic solvent, such as an alcohol. In the hydroformylation of olefins, typically an alcohol is selected which is identical or similar to an alcohol as obtained in the hydroformylation reaction.

[0045] The amount of solvent to be used in the process of the invention may vary considerably. It is within the reach of those skilled in the art to establish in each case the degree of cooling and the optimal amount of solvent required for the formation of a multiphase liquid reaction medium. The experimental results provided hereinafter, are also indicative for the amount of solvent, preferably to be used.

[0046] The process of the invention is eminently suitable to be used for the preparation of alcohols from internal olefins at high rate, in particular by using a catalyst system as defined above, based on palladium as the platinum group metal.

[0047] Furthermore the process is very useful for the preparation of aldehydes having a high linearity, in particular by using a catalyst system as defined above, based on platinum as platinum group metal.

[0048] The invention will be illustrated by the following examples. The abbreviations have the following meanings:

BCPE = 1,2-bis(1,4-cyclooctylenephosphino)ethane

TFSA = trifluoromethanesulphonic acid

EH = 2-ethylhexan-1-ol

Examples

5 [0049] In the Examples, the hydroformylation of an C₁₁/C₁₂ olefin mixture, isomerised to equilibrium (i.e. mainly internal linear olefins), with carbon monoxide and hydrogen in the presence of a Pd/BCPE/TFSA catalyst composition and varying amounts of chloride and water was followed by analysing samples by Gas Chromatography (GC).

[0050] At the end of the reaction (the duration of which depends on the activity of the catalytic system) the selectivity to the C₁₂/C₁₃ alcohol end-product was >98 mol%, the linearity of the alcohols produced was 75 mol% and the
10 amounts of paraffins produced less than 1 mol% in all cases.

[0051] The differences between the results are in the activity, as expressed by the first-order reaction rate constant k. Assuming that the conversion of olefin to alcohol is of first order in both the olefin and the metal (Pd), k is expressed per hour per mol Pd and calculated for batch operation according to the formula

$$15 \quad k = -(1/[Pd]) \cdot \ln\{(100-X)/t\}$$

wherein [Pd] is the mol amount of Pd used, X the mol% of olefin converted and t the time in hours.

Example 1 (NaCl/Pd = 0.1; H₂O = 0.6 wt%)

20 [0052] An experiment was carried out in a 300 ml stirred batch autoclave. The autoclave was charged with 77.68 ml C₁₁/C₁₂ isomerised olefin, 64.47 ml EH, and 0.81 ml water. After being flushed the autoclave was pressurised with hydrogen and carbon monoxide in a molar ratio of 2:1 to a pressure of 5000 kPa and heated to 105 °C. The catalyst solution (0.475 mmol palladium(II)acetate, 0.665 mmol BCPE, 0.0475 mmol NaCl, and 1.09 mmol TFSA dissolved in
25 16.4 ml sulfolane) was added to the content of the autoclave.
Reaction rate constant k = 950

Example 2 (NaCl/Pd = 0.3; H₂O = 0.6 wt%)

30 [0053] An experiment was carried out substantially as in Example 1, with the difference that 0.143 mmol NaCl was used.
Reaction rate constant k = 2200

Example 3 (NaCl/Pd = 0.8; H₂O = 0.6 wt%)

35 [0054] An experiment was carried out substantially as in Example 1, with the difference that 0.38 mmol NaCl was used.
Reaction rate constant k = 650

40 Example 4 (NaCl/Pd = 0.3; H₂O = 1.6 wt%)

[0055] An experiment was carried out substantially as in Example 1, with the difference that 2.16 ml water was applied and that the catalyst solution consisted of 0.25 mmol palladium(II)acetate, 0.3 mmol BCPE, 0.075 mmol NaCl, and 0.575 mmol TFSA dissolved in 16.4 ml sulfolane.

45 Reaction rate constant k = 2200

Example 5 (NaCl/Pd = 0.43; H₂O = 1.6 wt%)

50 [0056] An experiment was carried out substantially as in Example 4, with the difference that 0.108 mmol NaCl was used.
Reaction rate constant k = 3200

Example 6 (NaCl/Pd = 0.7; H₂O = 1.6 wt%)

55 [0057] An experiment was carried out substantially as in Example 4, with the difference that 0.175 mmol NaCl was used.
Reaction rate constant k = 2600

Example 7 (NaCl/Pd = 0.3; H₂O = 2.4 wt%)

[0058] An experiment was carried out substantially as in Example 1, with the difference that 0.143 mmol NaCl and 3.24 ml water was used.

5 Reaction rate constant k = 3500

Example 8 (NaCl/Pd = 0.55; H₂O = 2.4 wt%)

[0059] An experiment was carried out substantially as in Example 1, with the difference that 0.261 mmol NaCl and 3.24 ml water was used.

10 Reaction rate constant k = 4100

Example 9 (NaCl/Pd = 0.8; H₂O = 2.4 wt%)

[0060] An experiment was carried out substantially as in Example 1, with the difference that 0.38 mmol NaCl and 3.24 ml water was used.

Reaction rate constant k = 3300

[0061] These Examples and their results are summarised in the following Table.

Table

Example No.	NaCl/Pd	H ₂ O, wt%	Reaction rate constant k
1	0.1	0.6	950
2	0.3	0.6	2200
3	0.8	0.6	650
4	0.3	1.6	2200
5	0.43	1.6	3200
6	0.7	1.6	2600
7	0.3	2.4	3500
8	0.55	2.4	4100
9	0.8	2.4	3300

[0062] From these results it may be concluded, that the addition of water above 0.6 wt% enhances the activity-promoting effect of the halide. The halide/metal molar ratio at which maximum activity is observed is raised as well.

Claims

1. A process for the hydroformylation of ethylenically unsaturated compounds with carbon monoxide and hydrogen in the presence of a catalyst system comprising

- a) a source of platinum group metal cations;
- b) a source of non-halide anions;
- c) a source of at least one bidentate ligand of the formula



wherein M¹ and M² independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent bridging group containing from 1-4 atoms in the bridge, R¹ and R² independently represent a substituted or unsubstituted hydrocarbyl group, or together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M¹, and R³ and R⁴ independently represent a substituted or unsubstituted hydrocarbyl group, or together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M²; and

- d) a source of halide anions chosen from the group of chloride, iodide and bromide and mixtures thereof, char-

acterised by the additional presence of water, in an amount of more than 0.6 wt% based on the total of the reaction mixture and up to its solubility limit under the reaction conditions.

- 5 2. A process according to claim 1, characterised in that the molar ratio between the halide anions and the platinum group metal cations is between 0.02:1 and 3:1.
3. A process according to claim 1 or 2, characterised in that a) is a source of palladium or platinum cations.
- 10 4. A process according to any one of claims 1-3, characterised in that b) is a strong acid having a pKa below 3.
5. A process according to any one of claims 1-4, characterised in that in the bidentate ligand of formula (I) both of M^1 and M^2 are phosphorus and R is CH_2-CH_2 or $CH_2-CH_2-CH_2$.
- 15 6. A process according to any one of claims 1-5, characterised in that in the bidentate ligand of formula (I) each of the bivalent cyclic groups, represented by R^1 together with R^2 and R^3 together with R^4 respectively, is a cycloalkylene group having from 6 to 9, preferably 8, ring atoms.
7. A process according to any one of claims 1-6, characterised in that the halide anion is a chloride.
- 20 8. A process according to any one of claims 1-7, characterised in that the amount of water is between 0.7-3.0 wt%, based on the total of the reaction mixture.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,Y	WO 95 05354 A (SHELL INT RESEARCH) 23 February 1995 * the whole document *	1-8	C07C45/50 C07C29/16
Y	US 5 288 918 A (MAHER JOHN M ET AL) 22 February 1994 * claims 1-5 *	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 November 1998	Examiner Bonnevalle, E
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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Abstract

A fluid is provided for reducing differences in the permeability of a heterogeneous or fissured geological formation through which runs a well linked to the surface. The fluid consists of a stable suspension of solid particles and is selectively injected into areas of high permeability or into fissures rather than into areas of low permeability. Said suspension can be used to treat water inflows in production wells and to improve injection recovery in a productive formation. A method for reducing differences in the permeability of a geological formation is also provided.

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